



1 **Decoupling phosphorus availability and fixation in tropical soils: roles of**  
2 **iron and aluminum oxides across agroecological gradients in Nigeria**

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14 **Abstract**

15 Phosphorus (P) deficiency and fixation are major constraints to crop productivity in tropical  
16 soils, yet their large-scale interactions remain poorly understood. This study provides a  
17 national-scale assessment of how short-range-ordered iron (Fe<sub>ox</sub>) and aluminum (Al<sub>ox</sub>) oxides,  
18 soil properties, and climate jointly regulate P availability across Nigeria. A total of 1,382 topsoil  
19 samples (0–20 cm), collected using a hierarchical Soils4Africa framework, were analyzed for  
20 extractable P, Fe<sub>ox</sub>, Al<sub>ox</sub>, soil organic carbon (SOC), texture, and pH, and integrated with  
21 precipitation data. We developed a phosphorus sorption index (PSI) to quantify fixation  
22 potential as the molar ratio of oxide abundance to available P. Soil properties varied strongly  
23 along agroecological gradients, with Fe<sub>ox</sub>, Al<sub>ox</sub>, SOC, precipitation, and PSI increasing from  
24 semi-arid savannas to humid forest systems, while pH declined. Contrary to the expected  
25 inverse relationship, extractable P was positively associated with Fe<sub>ox</sub>, Al<sub>ox</sub>, SOC, and  
26 precipitation, but negatively related to PSI. Multivariate analyses clarified this apparent  
27 paradox: SOC exerted the strongest positive effect on P availability, whereas Al<sub>ox</sub> had a strong  
28 negative effect consistent with sorption, and precipitation influenced P both directly and  
29 indirectly through oxide accumulation. These results demonstrate that P availability and  
30 fixation are not simply inversely coupled but are co-regulated by climatic and biological  
31 processes. The PSI effectively captured spatial variation in fixation potential, with the highest  
32 values in humid regions characterized by intensive weathering. These findings highlight the  
33 dominant role of agroecological gradients in structuring P dynamics and reveal contrasting  
34 nutrient constraints across regions: oxide-rich humid soils are limited by fixation, whereas  
35 northern savannas are constrained by low inherent P. This study provides a mechanistic basis  
36 for site-specific phosphorus management and supports the development of sustainable nutrient  
37 strategies to improve P-use efficiency in tropical agroecosystems.

38 **Keywords:** Phosphorus availability; phosphorus fixation; iron and aluminum oxides; soil  
39 organic carbon; tropical soils; nutrient-use efficiency; site-specific management; Nigeria

40

41 **1. Introduction**

42 Phosphorus (P) deficiency remains one of the most persistent constraints to crop productivity  
43 in tropical soils, limiting agricultural output and contributing to food insecurity across Sub-



44 Saharan Africa (Sanchez, 2019). In many regions, particularly the Sahel, alleviating P  
45 deficiency is a prerequisite for effective use of other nutrients and for achieving sustainable  
46 yield gains (Horst et al., 2001; Jibrin et al., 2002). Unlike nitrogen, which benefits from  
47 biological fixation and atmospheric inputs, phosphorus is derived primarily from the  
48 weathering of parent material and is characterized by low mobility and slow replenishment in  
49 soils (Roy et al., 2006). These inherent constraints result in low fertilizer-use efficiency, as a  
50 substantial proportion of applied P becomes rapidly immobilized, increasing both economic  
51 costs and environmental risks associated with nutrient management.

52 Sorption of phosphate onto iron (Fe) and aluminum (Al) oxides and hydroxides represents a  
53 central mechanism controlling P availability in tropical soils. Both crystalline and short-range-  
54 ordered phases exhibit strong affinity for phosphate ions, forming stable inner-sphere  
55 complexes that reduce P solubility and plant availability (Parfitt, 1978; Gerard, 2016). Short-  
56 range-ordered Fe and Al oxides are particularly influential due to their high surface area and  
57 abundance of reactive sorption sites (Schwertmann and Taylor, 1989; Asomaning, 2020).  
58 Oxalate-extractable Fe and Al ( $Fe_{ox}$  and  $Al_{ox}$ ) are widely used as proxies for these reactive  
59 phases and have been shown to correlate strongly with phosphorus sorption capacity in tropical  
60 soils (Borggaard, 1983; van der Zee and van Riemsdijk, 1988). However, most existing  
61 knowledge is derived from site-specific studies, leaving uncertainty about how these  
62 mineralogical controls operate across heterogeneous landscapes.

63 Highly weathered soils such as Ferralsols, Acrisols, and Nitisols dominate large parts of Sub-  
64 Saharan Africa and are characterized by low inherent fertility and high phosphorus fixation  
65 capacity (Buresh et al., 1997; Sanchez, 2019). In these systems, the efficiency of applied  
66 phosphate fertilizers is often low because a substantial fraction of added P is rapidly sorbed  
67 onto soil mineral surfaces (Mutwale et al., 2023). Poor fertilizer recovery contributes to  
68 persistent nutrient limitations in smallholder farming systems and reinforces low productivity  
69 and soil degradation (Roy et al., 2006; Magnone et al., 2022). At the same time, increasing  
70 evidence indicates that the relationship between oxide abundance and plant-available P is not  
71 uniformly negative. Soils with high concentrations of reactive Fe and Al phases can also exhibit  
72 relatively high levels of extractable P, reflecting the influence of organic matter inputs,  
73 microbial activity, and P recycling processes (Hinsinger, 2001; Haynes and Mokolobate, 2001;  
74 Reed et al., 2015). These observations suggest that phosphorus availability and fixation may  
75 be co-regulated by interacting climatic, biological, and mineralogical processes rather than  
76 being simply inversely coupled.

77 Nigeria provides a unique setting to examine these interactions across strong environmental  
78 gradients. The country spans a wide range of agroecological zones, from humid forest systems  
79 in the south to Sudan and Sahel savannas in the north, encompassing marked differences in  
80 precipitation, weathering intensity, and soil development (Yahmed, 2002). These gradients  
81 generate soils with contrasting mineralogical and chemical properties, including oxide-rich,  
82 highly weathered soils in humid regions and sandy, weakly developed soils in arid zones  
83 (FDALR, 1990). This diversity creates a natural gradient for evaluating how the balance  
84 between P supply and fixation varies across climatic and pedogenic conditions. Despite this  
85 variability, phosphorus deficiency remains widespread across Nigerian farming systems,  
86 contributing to low fertilizer-use efficiency and constrained agricultural productivity  
87 (Osemwotai et al., 2005; Rurinda et al., 2020).

88 Current understanding of phosphorus dynamics in Nigeria is limited by the lack of national-  
89 scale, quantitative assessments linking oxide mineralogy to P availability across agroecological



90 zones. Most studies have focused on local or experimental sites, often targeting specific soil  
91 types or management conditions (Osemwotai et al., 2005; Ibia and Udo, 1993). As a result, the  
92 extent to which phosphorus availability and fixation are coupled or decoupled across large  
93 tropical gradients remains unresolved. Addressing this gap is essential for improving fertilizer  
94 recommendations, which often remain generalized and fail to account for spatial variation in  
95 soil properties and nutrient constraints (Rurinda et al., 2020).

96 Recent advances in large-scale soil data collection provide new opportunities to address this  
97 challenge. Harmonized datasets generated through efforts such as the Soils4Africa project  
98 include measurements of key soil properties across diverse environmental conditions,  
99 including short-range-ordered Fe and Al oxides, soil texture, organic carbon, and plant-  
100 available phosphorus. These datasets enable integrated analysis of mineralogical, climatic, and  
101 biological controls on P dynamics at spatial scales relevant for national and regional decision-  
102 making. Understanding the spatial distribution of phosphorus fixation potential, and its  
103 interaction with P availability, is critical for developing efficient and sustainable nutrient  
104 management strategies. Identification of regions where fixation processes dominate, as  
105 opposed to areas where P supply is limiting, can support targeted interventions that improve  
106 fertilizer-use efficiency, reduce input costs, and minimize environmental impacts. Such  
107 approaches are central to sustainable intensification in tropical agroecosystems.

108 This study uses harmonized soil property data from the Soils4Africa project to investigate how  
109 short-range-ordered iron and aluminum oxides regulate phosphorus availability across  
110 Nigeria's agroecological landscapes. The analysis (i) quantifies relationships between oxalate-  
111 extractable Fe and Al and plant-available P while accounting for key soil properties, including  
112 pH, clay content, and soil organic carbon; (ii) develops a phosphorus sorption index (PSI) that  
113 integrates oxide abundance with available P to estimate fixation potential; and (iii) maps the  
114 spatial distribution of P fixation across agroecological zones. The study tests the hypothesis  
115 that oxide-rich soils exhibit strong sorption capacity but do not necessarily exhibit reduced P  
116 availability due to co-regulation by climatic and biological processes, that the combined  
117 abundance of short-range-ordered Fe and Al oxides provides a robust predictor of fixation  
118 potential, and that spatial patterns of P dynamics follow gradients in weathering intensity, soil  
119 properties, and climate. This work advances a mechanistic framework for understanding the  
120 co-regulation of phosphorus availability and fixation and provides a foundation for developing  
121 site-specific, sustainable phosphorus management strategies in tropical agroecosystems.

## 122 **2 Methodology**

### 123 **2.1 Study Area**

124 Nigeria is located in West Africa between 4°-14°N and 3°-15°E, covering approximately  
125 923,770 km<sup>2</sup> of land and encompassing diverse climatic and geological environments that  
126 influence soil formation and nutrient dynamics (Yahmed, 2002; IIASA/FAO, 2012). The  
127 country spans several agro-ecological zones, including the humid forest, derived savanna,  
128 southern Guinea Savanna, northern Guinea Savanna, mid-altitude highlands, Sudan Savanna  
129 and Sahel Savanna, characterized by strong rainfall gradients from >2000 mm in the south to  
130 less than 600 mm in the northern Sahel. Figure 1 shows the agroecological zones and the  
131 dominant geological formations. Nigeria's geology is dominated by the Precambrian Basement  
132 Complex (granites, gneisses, migmatites, and schists) and several sedimentary basins,  
133 including the Niger Delta, Benue Trough, Chad Basin, Sokoto Basin, and Bida Basin (Yahmed,  
134 2002; Tijani, 2023). Basement-derived soils are typically strongly weathered and enriched in  
135 iron and aluminium oxides, whereas soils developed on sedimentary formations often contain



136 lower sesquioxide concentrations. These environmental gradients have produced diverse soil  
137 groups, including Ferralsols, Acrisols, Lixisols, and Luvisols, whose mineralogical  
138 composition strongly influences phosphorus sorption and availability in Nigerian agricultural  
139 soils (FDALR, 1990).

## 140 **2.2 Soil sampling design and field sampling procedure**

141 Soil sampling followed the Soils4Africa field survey protocol (Huising and Mesele, 2022),  
142 which applies a standardized hierarchical sampling framework to ensure spatial  
143 representativeness across agricultural landscapes (Kempen et al., 2021). The sampling design  
144 consisted of three nested levels. Primary Sampling Units (PSUs) were defined as  $2 \times 2$  km grid  
145 cells, within which Secondary Sampling Units (SSUs) of 1 ha were randomly selected. Within  
146 each SSU, Tertiary Sampling Units (TSUs) of 25 m<sup>2</sup> were established as the operational soil  
147 sampling plots. Within each TSU, soil samples were collected from four subsampling locations  
148 arranged in a Y-shaped configuration, consisting of one central point and three peripheral  
149 points located approximately 2 m from the centre and spaced equidistantly. Composite surface  
150 (0–20 cm) samples collected from 1382 TSUs across Nigeria (figure 1) were used for this study.

## 151 **2.3 Mid-infrared (MIR) spectral analysis of soil samples**

152 MIR spectra were collected using a Bruker ALPHA II FT-IR spectrometer equipped with a  
153 DRIFTS module, ZnSe beamsplitter, and DTGS detector. Finely ground (<0.5 mm) soil was  
154 packed into 6-mm stainless steel micro-cups and levelled with a spatula before scanning.  
155 Spectra were acquired using OPUS software over 4000–400 cm<sup>-1</sup> wavenumbers, with  
156 resolution: 8 cm<sup>-1</sup>, 32 co-added scans and ~1705 wavenumber data points.

157 According to ICRAF soil spectral library protocols (Tchikoui et al., 2019; Viscarra Rossel et  
158 al., 2016), instrument performance was routinely evaluated using a gold reflectance reference  
159 and three ICRAF calibration soils (Katumani, White Sands, Heavy Black Cracking Clay).  
160 Background spectra were collected on the gold standard and ZnSe optics were checked  
161 routinely. Data were reported as absorbance ( $\log_{10}$  of inverse reflectance).

162 Raw spectra were visually inspected for CO<sub>2</sub> interference, water absorption, baseline curvature,  
163 or aberrant shapes inconsistent with typical soil MIR signatures. Suspect spectra were  
164 re-scanned. Replicate precision was assessed by computing the coefficient of variation (CV)  
165 across duplicate spectra; absorbance values with CV > 1% (Stenberg et al., 2010) were flagged  
166 as outliers and re-measured. Only spectra meeting QC thresholds were retained for modelling.  
167 For pre-processing and chemometric modeling, OPUS spectra were exported as ASCII files  
168 and converted into a sample-by-wavenumber matrix. Pre-processing in R (version 4.4.3, R  
169 Core Team, 2024) included: rubber-band baseline correction, Savitzky–Golay (Savitzky &  
170 Golay, 1964). (smoothing (11-point, 2nd-order), mean-centering and unit-variance scaling,  
171 removal of atmospheric interference regions ( $\approx 2400$ – $2300$  cm<sup>-1</sup>,  $1900$ – $1800$  cm<sup>-1</sup>) and  
172 Savitzky–Golay derivatives to enhance spectral features

173 ICRAF spectral processing scripts were used for standardized treatment, including scatter  
174 correction and region selection. Calibration models were developed using Partial Least Squares  
175 (PLS) regression (Martens & Naes, 1989) and Random Forest (RF) (Breiman, 2001), with 20%  
176 hold-out validation. The MIR-DRIFTS workflow follows established chemometric best  
177 practices, enabling simultaneous prediction of multiple soil properties from high-quality  
178 reference datasets.

179 The calibration subset (20% of the total samples) was strategically selected using the Kennard-  
180 Stone algorithm based on the MIRS spectral data. This ensures that the full spectral variability



181 of the entire sample set was captured within the calibration subset. These selected samples were  
182 subjected to standard laboratory wet chemical analysis.

#### 183 **2.4 Wet Chemistry analysis of soil samples**

184 Soil chemical and physical properties were determined using standardized analytical  
185 procedures. Soil pH was measured potentiometrically in water suspension (1:5 soil-to-solution  
186 ratio) using a calibrated glass electrode pH meter, following ISO 10390:2005, while electrical  
187 conductivity (EC) was measured in a 1:5 soil–water extract at 25 °C using a temperature-  
188 compensated conductivity meter (ISO 11265:1994). Exchangeable acidity ( $H^+ + Al^{3+}$ ) was  
189 determined following 1 M KCl extraction and titration (McLean, 1965). Plant-available  
190 phosphorus (P) was extracted using the Mehlich III method and quantified by inductively  
191 coupled plasma optical emission spectrometry (ICP-OES) (Mehlich, 1984). Soil organic matter  
192 was determined by dry combustion at 900 °C, with organic carbon derived from total carbon  
193 measurements (Nelson & Sommers, 1996). Short-range-ordered Fe and Al were extracted  
194 using acid ammonium oxalate under dark conditions and quantified by ICP-OES, providing an  
195 estimate of reactive oxide phases (Warren, 1994). Soil texture was determined using the  
196 Bouyoucos hydrometer method, with particle-size fractions classified according to ISO  
197 11277:2009.

#### 198 **2.5 Quantification of phosphorus sorption index**

199 To quantify soil P fixation and P supply potentials, the following pedotransfer function was  
200 calculated to give the Phosphorus Sorption Index (PSI) based on the relative abundance of  
201 amorphous Al and Fe oxides to extractable phosphorus.

$$202 \quad \text{PSI} = \frac{\left(\frac{Al_{ox}}{27} + \frac{Fe_{ox}}{56}\right)}{\left(\frac{P}{31}\right)}$$

203 where:

204  $Al_{ox}$ ,  $Fe_{ox}$ , and  $P$  are concentrations in  $mg\ kg^{-1}$ , 27, 56, and 31 represent the atomic weights  
205 ( $g\ mol^{-1}$ ) of Al, Fe, and P, respectively. This index normalizes P-sorbing mineral abundance  
206 by available P concentration, thereby providing a mechanistically meaningful indicator of soil  
207 P fixation potential. Higher PSI values indicate a greater dominance of amorphous oxides  
208 relative to available P and, consequently, a higher likelihood of P immobilization.

#### 209 **2.6 Statistical Analysis**

210 Descriptive statistics were computed for all soil and climatic variables. Results are reported as  
211 mean  $\pm$  standard deviation, along with sample size (N). Normality of continuous variables was  
212 evaluated using the Shapiro–Wilk test. Variables exhibiting right-skewed distributions (P,  $Al_{ox}$ ,  
213  $Fe_{ox}$ , PSI, and precipitation) were log-transformed prior to inferential analysis.

214 Pearson correlation coefficients were computed among variables. Multiple linear regression  
215 (MLR) was used to quantify the relative influence of soil properties and precipitation on  
216 extractable phosphorus:

$$217 \quad \log(P) = \beta_0 + \beta_1 \log(Al_{ox}) + \beta_2 \log(Fe_{ox}) + \beta_3 pH + \beta_4 SOC + \beta_5 Clay + \beta_6 \log(Precip) \\ 218 \quad + \beta_7 (pH \times \log(Al_{ox})) + \varepsilon$$



219 where:

220  $\beta_i$  are regression coefficients and  $\varepsilon$  is the error term.

221 Structural Equation Modeling (SEM) was employed to further disentangle direct and indirect  
222 pathways influencing extractable P. The hypothesized SEM assumed that short-range-ordered  
223 Al and Fe oxides exert direct control on P availability; and soil pH and precipitation influence  
224 P indirectly by regulating oxide formation and reactivity.

225 *Spatial Analysis and Geostatistical Modeling*

226 All spatial analyses were conducted in UTM Zone 32N (EPSG: 32632) to ensure distance-  
227 based geostatistical validity.

228 An empirical variogram was computed for log-transformed PSI:

230 
$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i) - Z(x_i + h)]^2$$

229

231 Optimal theoretical variogram models were selected using automated fitting procedures.  
232 Ordinary kriging was applied to interpolate PSI across Nigeria:

234 
$$\hat{Z}(x_0) = \sum_{i=1}^n \lambda_i Z(x_i)$$

233

235 where  $\lambda_i$  are kriging weights determined by the variogram model. A local neighborhood  
236 (maximum 50 nearest observations) was specified to ensure stable predictions. Geostatistical  
237 interpolation enables visualization of spatial patterns in P fixation potential and supports  
238 regional soil fertility management planning.

239 All analyses were conducted in **R** version 4.4 (R Core Team, 2023) and QGIS (version LTR  
240 3.44.8).

## 241 **3.0 Results & Discussion**

### 242 **3.1 Agroecological controls on soil properties and phosphorus dynamics**

243 Soil properties exhibited strong and systematic variation across agroecological zones (AEZs),  
244 reflecting a clear gradient from the Sahel and Sudan Savanna to the Humid Forest (Tables 1  
245 and 2). Available P increased from 8.99 mg kg<sup>-1</sup> in the Sahel and 9.36 mg kg<sup>-1</sup> in the Sudan  
246 Savanna to 15.56 mg kg<sup>-1</sup> in the Humid Forest, with intermediate values across the Guinea and  
247 Derived Savanna zones. Oxalate-extractable Al and Fe (Al<sub>ox</sub> and Fe<sub>ox</sub>) followed a similar trend,  
248 increasing from 259.14 and 438.48 mg kg<sup>-1</sup> in the Sahel to 1295.68 and 1666.22 mg kg<sup>-1</sup> in the  
249 Humid Forest. Soil organic carbon (SOC) increased from 0.27% to 1.52%, while pH declined  
250 from 6.39 to 5.31. Precipitation increased from 714.47 mm to 2191.90 mm, closely mirroring  
251 oxide accumulation and PSI, which increased from 66.80 to 184.64. The spatial distribution of



252 these properties is shown in figures 2-4. These trends reflect increasing weathering intensity,  
253 leaching, and accumulation of secondary Fe and Al oxides under higher rainfall conditions.  
254 Tropical soil development is strongly governed by climate, particularly rainfall, which controls  
255 mineral transformation, organic matter dynamics, and nutrient redistribution (Jenny, 1941;  
256 Tardy, 1997; Sanchez, 2019). The strong AEZ effect confirmed by two-way ANOVA results  
257 (Supplementary Table S1) indicates that climate-driven pedogenesis is the dominant control  
258 on soil properties at the national scale.

### 259 3.1 Geological Influence and interaction with agroecology

260 Variation across geological formations was evident but less systematic than across AEZs  
261 (Table 2). Available P ranged from 7.77 mg kg<sup>-1</sup> in the Chad Formation to 18.84 mg kg<sup>-1</sup> in  
262 Tertiary volcanic formations, while Al<sub>ox</sub> and Fe<sub>ox</sub> were highest in oxide-rich formations such as  
263 Tertiary Volcanics, Asu River Group, and Nkporo Shale. PSI exceeded 200 in these formations  
264 but remained below 70 in sandy formations, indicating strong contrasts in fixation potential.  
265 Grouping formations by geological age revealed moderate differences (Table 3), with  
266 substantial within-group variability. While parent material influences baseline mineral  
267 composition, its effects are moderated by weathering and pedogenic processes. This is  
268 confirmed by the two-way ANOVA (Supplementary Table S1), which shows that geology has  
269 significant effects only on selected variables, whereas AEZ × geology interactions are highly  
270 significant for all variables ( $p < 0.001$ ). These interactions demonstrate that the influence of  
271 parent material is strongly conditioned by agroecological context, consistent with classical soil  
272 formation theory (Jenny, 1941) and tropical weathering processes (Tardy, 1997).

### 273 3.2 Relationships among soil properties

274 Pearson correlation analysis revealed strong interrelationships among soil variables (Fig. 5).  
275 Available P was positively correlated with SOC ( $r = 0.55$ ), Al<sub>ox</sub> ( $r = 0.35$ ), Fe<sub>ox</sub> ( $r = 0.35$ ), and  
276 precipitation ( $r = 0.25$ ), while PSI was negatively correlated with P ( $r = -0.18$ ). Strong  
277 correlations between Al<sub>ox</sub> and Fe<sub>ox</sub> ( $r = 0.83$ ) and between SOC and oxide fractions reflect their  
278 shared dependence on weathering intensity and soil development. Principal component  
279 analysis (Fig. 6) further demonstrated clear clustering by agroecological zone, with Humid  
280 Forest soils associated with high precipitation, SOC, and oxide concentrations, and  
281 Sahel/Sudan soils occupying contrasting positions. Geological groupings were less distinct,  
282 reinforcing the dominant role of climate. These results show that soil properties co-vary along  
283 environmental gradients, with precipitation acting as a key driver linking oxide formation,  
284 organic matter accumulation, and soil texture.

### 285 3.3 Decoupling phosphorus availability and fixation

286 A key finding of this study is that phosphorus availability and fixation are not simply inversely  
287 related. Available P showed positive correlations with Al<sub>ox</sub>, Fe<sub>ox</sub>, SOC, and precipitation, while  
288 PSI was negatively correlated with P (Fig. 5). This indicates that oxide-rich environments can  
289 simultaneously exhibit high fixation potential and relatively higher extractable P. This apparent  
290 contradiction arises from the co-regulation of P dynamics by multiple processes. In humid  
291 environments, increased rainfall enhances both oxide formation and biological activity, leading  
292 to higher organic matter inputs and more active P cycling. Consequently, P availability reflects  
293 the balance between sorption, mineralization, and biological recycling rather than sorption  
294 alone (Hinsinger, 2001; Vance et al., 2003; Haynes and Mokolobate, 2001). The role of oxides  
295 in P fixation is well established, particularly for amorphous Fe and Al phases, which provide



296 reactive surfaces for phosphate adsorption (Parfitt, 1978; Sanyal and De Datta, 1991;  
297 Schwertmann and Taylor, 1989). However, the positive correlation between oxides and  
298 available P indicates that these processes are embedded within broader pedogenic and  
299 ecological systems.

### 300 **3.4 Mechanistic controls on phosphorus availability**

301 Multivariate analyses provided further insight into the mechanisms controlling P availability.  
302 The regression model (Table 4) explained a substantial proportion of variance (adjusted  $R^2 =$   
303 0.63), with SOC as the strongest positive predictor and clay content exerting a negative effect.  
304 The Humid Forest and Southern Guinea Savanna were associated with higher P levels, while  
305 Jurassic and Tertiary formations also showed positive effects. A significant  $Al_{ox} \times pH$   
306 interaction indicates that oxide-mediated sorption is influenced by soil acidity. The structural  
307 equation model (Fig. 7) further disentangled these relationships. SOC had the strongest positive  
308 direct effect on P, highlighting the role of organic matter in enhancing P availability through  
309 mineralization and competitive sorption. In contrast,  $Al_{ox}$  exerted a strong negative effect,  
310 confirming its role as a dominant sorption phase.  $Fe_{ox}$  showed a moderate positive effect,  
311 suggesting that it reflects broader pedogenic conditions rather than acting solely as a sorption  
312 agent. Precipitation played a central role, strongly influencing  $Al_{ox}$  and  $Fe_{ox}$  accumulation and  
313 exerting both direct and indirect effects on P availability. Soil pH had smaller indirect effects,  
314 primarily through its influence on oxide formation. These findings align with previous studies  
315 showing that P dynamics in tropical soils are controlled by interacting climatic, mineralogical,  
316 and biological processes (Gerard, 2016; Hinsinger, 2001).

### 317 **3.5 PSI as an integrative indicator**

318 The phosphorus sorption index (PSI) effectively integrates oxide abundance and available P,  
319 providing a robust indicator of fixation potential. Its strong increase across AEZs (Table 1 and  
320 Fig. 4) and close association with oxide concentrations demonstrate its utility for mapping  
321 fixation risk. The lack of a significant independent geological effect on PSI, combined with  
322 strong  $AEZ \times geology$  interactions (Table 4), indicates that fixation potential is primarily  
323 controlled by pedogenic processes rather than parent material alone. This supports the view  
324 that P limitation intensifies with increasing weathering and oxide accumulation (Parfitt and  
325 Smart, 1978; Borggaard, 1983).

### 326 **3.6 Implications for sustainable phosphorus management**

327 The contrasting patterns observed across agroecological zones have direct implications for  
328 sustainable P management and nutrient-use efficiency in tropical agroecosystems. In humid  
329 and subhumid regions, where PSI values are high and oxide concentrations are elevated, P  
330 limitation is primarily driven by fixation processes. In these environments, improving P-use  
331 efficiency requires strategies that reduce sorption losses and enhance biological cycling.  
332 Increasing SOC is particularly critical, as it emerged as the strongest positive determinant of P  
333 availability. Organic amendments such as manure, compost, and crop residues can mitigate  
334 fixation through competitive sorption, complexation of reactive Al and Fe phases, and  
335 stimulation of microbial P mineralization (Menezes-Blackburn et al., 2018; Vanlauwe et al.,  
336 2015). Complementary practices, including localized fertilizer placement, liming to moderate  
337 soil acidity, and the use of P-efficient crop varieties, can further improve fertilizer recovery  
338 and reduce losses.



339 In contrast, soils of the Sahel and Sudan Savanna are characterized by low PSI and low inherent  
340 P levels, indicating that P limitation is primarily due to insufficient supply rather than strong  
341 sorption. In these systems, increasing P input remains essential to overcome nutrient constraints  
342 and support crop productivity. However, responses to P fertilization are often constrained by  
343 co-limitation with other nutrients, particularly nitrogen, highlighting the importance of  
344 integrated soil fertility management strategies (Kihara et al., 2020; Rurinda et al., 2020). The  
345 coexistence of fundamentally different P constraints across regions underscores the limitations  
346 of generalized fertilizer recommendations and reinforces the need for site-specific approaches  
347 tailored to local soil conditions. More broadly, these findings contribute to sustainable  
348 intensification efforts by demonstrating that improving P-use efficiency requires simultaneous  
349 consideration of mineralogical constraints, organic matter dynamics, and climatic drivers. The  
350 PSI provides a practical tool for identifying areas with high fixation risk and guiding targeted  
351 interventions. Integration of such indices with agroecological zoning and soil information  
352 systems offers a pathway toward more efficient fertilizer use, reduced environmental impacts,  
353 and improved resilience of agricultural systems.

#### 354 **Conclusion**

355 This study provides a national-scale assessment of phosphorus (P) dynamics in tropical soils,  
356 showing that agroecological gradients, particularly climate-driven weathering and organic  
357 matter dynamics, are the primary controls on P availability and fixation across Nigeria.  
358 Geological effects are secondary and largely mediated through interactions with environmental  
359 conditions. The findings demonstrate that P availability and fixation are not simply inversely  
360 related but are co-regulated by mineralogical, climatic, and biological processes. Short-range-  
361 ordered aluminum plays a dominant role in P immobilization, while soil organic carbon  
362 strongly enhances P availability, highlighting the importance of organic matter in moderating  
363 P constraints. The phosphorus sorption index (PSI) developed in this study effectively captures  
364 spatial variation in fixation potential, distinguishing high-fixation humid systems from low-P,  
365 supply-limited savanna soils. These contrasting patterns indicate that P limitation arises from  
366 different mechanisms across agroecological zones and cannot be addressed through uniform  
367 fertilizer recommendations. Integrating PSI with agroecological zoning provides a practical  
368 basis for targeting interventions, improving P-use efficiency, and supporting sustainable  
369 intensification in tropical agroecosystems.

370

371 Ethical Approval

372 Not Applicable

373 Consent to Participate

374 Not Applicable

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378 Competing Interests

379 The authors declare that they have no known conflicts of interest.

380 Availability of data and materials

381 Data available publicly after the 2026 embargo period

382

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Table 1: Descriptive statistics of the variables by agroecological zones

	<b>Overall N = 1,382</b>	<b>Derived Savanna N = 363</b>	<b>Humid Forest N = 82</b>	<b>Northern Guinea Savanna N = 208</b>	<b>Sahel Savanna N = 76</b>	<b>Southern Guinea Savanna N = 276</b>	<b>Sudan Savanna N = 377</b>
Available P	11.88 ± 5.20	13.63 ± 4.94	15.56 ± 6.79	11.78 ± 5.31	8.99 ± 4.27	12.78 ± 4.64	9.36 ± 4.06
Al <sub>ox</sub>	594.63 ± 428.01	728.50 ± 441.52	1,295.68 ± 559.95	559.73 ± 294.97	259.14 ± 189.39	626.29 ± 360.44	376.95 ± 267.20
Fe <sub>ox</sub>	980.79 ± 748.66	1,230.41 ± 797.62	1,666.22 ± 761.24	981.82 ± 564.66	438.48 ± 404.16	1,052.77 ± 696.00	647.42 ± 649.29
pH	5.94 ± 0.42	5.94 ± 0.35	5.31 ± 0.39	6.00 ± 0.41	6.39 ± 0.32	5.89 ± 0.32	6.00 ± 0.43
OC	0.87 ± 0.57	1.21 ± 0.59	1.52 ± 0.48	0.83 ± 0.37	0.27 ± 0.21	0.99 ± 0.47	0.47 ± 0.32
Clay	19.03 ± 13.38	20.64 ± 13.13	30.45 ± 12.81	20.70 ± 13.01	11.82 ± 10.38	19.61 ± 12.99	15.10 ± 12.64
Precipitation (mm)	1,255.29 ± 345.88	1,347.61 ± 168.53	2,191.90 ± 484.35	1,209.11 ± 177.83	714.47 ± 83.66	1,313.26 ± 122.38	1,054.73 ± 170.65
PSI	109.83 ± 86.51	121.18 ± 97.32	184.64 ± 128.24	113.52 ± 70.69	66.80 ± 56.03	111.85 ± 81.56	87.80 ± 66.10

Al<sub>ox</sub> = Aluminium oxide; Fe<sub>ox</sub> = Iron oxide; OC = Organic carbon; PSI = Phosphorus sorption index. Significant differences were observed among the agroecological zones for all variables at p<0.05



Table 2 Variation in soil properties by geological formation

Geological Formation	N	Available P (mg kg <sup>-1</sup> )	Al <sub>ox</sub> (mg kg <sup>-1</sup> )	Fe <sub>ox</sub> (mg kg <sup>-1</sup> )	pH	Soil organic carbon (%)	Clay (%)	PSI
Abeokuta Formation	7	15.3 ± 4.63	828 ± 214	1250 ± 299	6.1 ± 0.23	1.5 ± 0.40	21.3 ± 9.26	113.62 ± 35.37
Asu River Group	15	11.6 ± 3.58	1161 ± 350	2093 ± 457	5.6 ± 0.33	1.3 ± 0.50	38.8 ± 5.4	238.58 ± 116.47
Awgu-Ndeaboh Shale Group	24	11.1 ± 2.46	661 ± 358	1207 ± 785	5.8 ± 0.29	1.0 ± 0.40	19.9 ± 12.60	132.84 ± 84.78
Basement Complex	616	12.8 ± 5.53	599 ± 305	1020 ± 555	6.0 ± 0.32	1.0 ± 0.51	19.2 ± 10.80	108.77 ± 68.18
Bima Sandstone and Yolde Formation	58	11.5 ± 3.46	505 ± 290	939 ± 584	6.2 ± 0.38	0.8 ± 0.31	18.2 ± 15.18	103.20 ± 77.87
Chad Formation	123	7.8 ± 2.16	219 ± 119	370 ± 258	6.3 ± 0.30	0.2 ± 0.12	9.4 ± 7.47	63.02 ± 43.19
Coastal Plains Sands	33	17.2 ± 6.69	1227 ± 450	1368 ± 371	5.2 ± 0.30	1.4 ± 0.40	25.9 ± 9.15	135.69 ± 51.48
Eze Aku Shale Group	50	11.7 ± 2.78	498 ± 327	875 ± 748	6.0 ± 0.29	0.8 ± 0.47	14.3 ± 10.53	90.05 ± 60.51
Falsebedded Sandstone and Upper Coal Measures	11	12.0 ± 3.86	1253 ± 982	1351 ± 795	5.5 ± 0.30	1.6 ± 0.95	28.0 ± 20.03	232.83 ± 261.51
Gombe Sandstone	21	9.7 ± 2.90	323 ± 154	560 ± 369	6.1 ± 0.19	0.5 ± 0.18	13.8 ± 11.31	79.65 ± 58.10
Gundumi Formation	19	9.1 ± 2.24	281 ± 147	353 ± 205	5.7 ± 0.38	0.3 ± 0.13	11.6 ± 8.38	60.63 ± 34.71
Gwandu Formation	44	8.2 ± 2.20	431 ± 294	533 ± 349	5.6 ± 0.30	0.4 ± 0.23	17.2 ± 14.02	104.05 ± 83.55
Ilaro Formation	4	15.2 ± 4.72	1036 ± 466	1419 ± 517	6.0 ± 0.36	1.9 ± 0.74	21.3 ± 10.37	141.29 ± 84.63
Illo Formation	28	9.7 ± 2.75	370 ± 166	539 ± 387	5.8 ± 0.22	0.6 ± 0.30	12.4 ± 5.73	79.80 ± 45.49
Imo Clay-Shale Group	7	12.8 ± 5.13	1163 ± 504	1612 ± 537	5.3 ± 0.39	1.3 ± 0.53	35.6 ± 14.94	181.59 ± 59.34
Kerri-Kerri Formation	60	9.2 ± 2.93	292 ± 88	352 ± 171	5.7 ± 0.18	0.4 ± 0.18	9.3 ± 5.14	62.69 ± 31.25
Lignite Formation	8	17.1 ± 5.49	1048 ± 562	1178 ± 467	5.3 ± 0.41	1.3 ± 0.42	21.9 ± 11.04	117.46 ± 68.05
Lower Coal Measures	8	16.2 ± 4.76	940 ± 443	1437 ± 507	6.0 ± 0.57	1.6 ± 0.59	28.1 ± 11.20	116.43 ± 45.88
Marine Facies Lafia Area	8	11.1 ± 2.03	304 ± 75	401 ± 143	6.0 ± 0.15	0.5 ± 0.14	5.6 ± 2.00	50.79 ± 6.23
Nkporo Shale Group	32	12.5 ± 4.44	1274 ± 875	1713 ± 961	5.6 ± 0.54	1.6 ± 0.80	34.4 ± 18.64	223.93 ± 182.74
Nupe Sandstones	48	11.9 ± 3.29	394 ± 137	611 ± 324	6.0 ± 0.15	0.7 ± 0.26	11.4 ± 6.49	70.32 ± 35.16
Pindiga Formation	33	12.9 ± 4.68	793 ± 387	1712 ± 1002	6.6 ± 0.52	0.9 ± 0.33	36.1 ± 18.80	161.76 ± 97.09
Rima Group	28	7.8 ± 2.02	360 ± 238	554 ± 563	5.8 ± 0.54	0.4 ± 0.24	16.6 ± 13.91	93.05 ± 67.81
Sokoto Group	9	13.7 ± 7.87	632 ± 311	984 ± 579	6.0 ± 0.52	0.7 ± 0.45	27.0 ± 17.16	111.44 ± 74.25
Sombreiro Deltaic Plain	4	12.0 ± 3.89	1079 ± 354	1592 ± 401	5.2 ± 0.31	1.5 ± 0.46	27.9 ± 3.95	179.02 ± 16.23
Tertiary to Recent Volcanics	16	18.8 ± 10.13	1282 ± 348	2543 ± 864	6.2 ± 0.70	1.6 ± 0.51	45.0 ± 9.32	181.14 ± 74.98
Younger Granites	13	13.53 ± 3.88	618 ± 330	918 ± 459	6.0 ± 0.49	0.8 ± 0.40	21.0 ± 13.72	95.55 ± 49.98



Table 3: Descriptive statistics of the soil variables by geological Age

Soil Property	Overall N = 1,382	Cretaceous N = 390	Jurassic N = 13	Pre-Cambrian to Upper Cambrian N = 616	Quaternary N = 214	Tertiary N = 149
Available P	11.88 ± 5.20	11.32 ± 3.68	13.53 ± 3.88	12.75 ± 5.53	10.89 ± 5.73	11.00 ± 5.91
Al <sub>ox</sub>	594.63 ± 428.01	603.57 ± 495.59	618.43 ± 329.62	598.57 ± 304.59	586.63 ± 568.82	564.35 ± 450.00
Fe <sub>ox</sub>	980.79 ± 748.66	991.25 ± 792.87	918.24 ± 458.49	1,020.16 ± 554.52	966.08 ± 1,053.51	817.23 ± 807.01
pH	5.94 ± 0.42	5.97 ± 0.46	6.01 ± 0.49	5.96 ± 0.32	6.00 ± 0.56	5.73 ± 0.42
OC	0.87 ± 0.57	0.85 ± 0.56	0.84 ± 0.40	0.99 ± 0.51	0.71 ± 0.66	0.68 ± 0.56
Clay	19.03 ± 13.38	19.79 ± 15.62	21.08 ± 13.72	19.17 ± 10.80	17.29 ± 14.05	18.79 ± 15.48
PSI	109.83 ± 86.51	116.65 ± 106.23	95.55 ± 49.98	108.77 ± 68.18	107.14 ± 102.02	101.51 ± 73.87

Al<sub>ox</sub> = Aluminium oxide; Fe<sub>ox</sub> = Iron oxide; OC = Organic carbon; PSI = Phosphorus sorption index. Significant differences were observed among the agroecological zones for all variables at p<0.05.



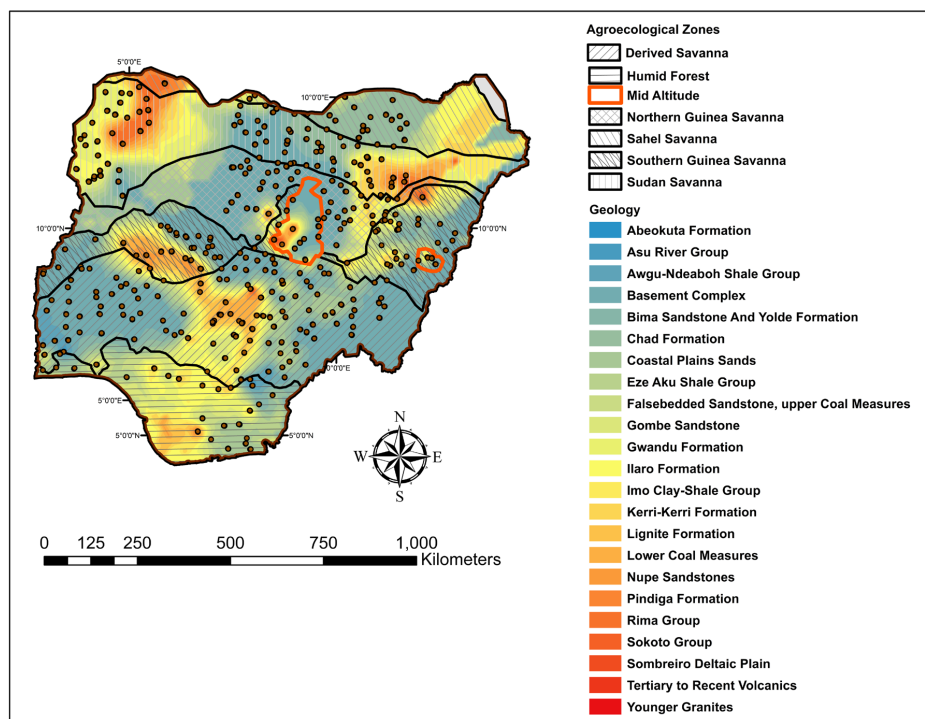
Table 4. Results of the multiple linear regression model predicting log-transformed plant-available phosphorus (P) as a function of soil properties, agroecological zones (AEZ), and geological formations.

Term	Estimate	Standard error	p-value	Lower confidence interval	Higher confidence interval
(Intercept)	0.410	1.059	0.699	-1.668	2.487
log_Al <sub>ox</sub>	0.016	0.160	0.920	-0.299	0.331
pH	0.018	0.169	0.917	-0.314	0.349
SOC	0.331	0.026	<b>0.000</b>	0.279	0.383
Clay	-0.017	0.001	<b>0.000</b>	-0.019	-0.015
AEZ:Humid Forest	0.194	0.037	<b>0.000</b>	0.122	0.265
AEZ:Northern Guinea	0.011	0.023	0.643	-0.035	0.056
AEZ:Sahel	-0.045	0.041	0.273	-0.126	0.036
AEZ:Southern Guinea	0.046	0.020	<b>0.025</b>	0.006	0.086
AEZ:Sudan	-0.026	0.024	0.281	-0.074	0.021
Geology:Jurassic	0.164	0.071	<b>0.021</b>	0.025	0.303
Geology:Pre-Cambrian to Upper Cambrian	0.001	0.017	0.940	-0.032	0.034
Geology:Quaternary	-0.005	0.026	0.834	-0.056	0.045
Geology:Tertiary	0.085	0.027	<b>0.002</b>	0.032	0.138
log_Al <sub>ox</sub> :pH	0.052	0.025	<b>0.041</b>	0.002	0.101

*Coefficients represent estimated effects ( $\beta$ ) with standard errors, p-values, and 95% confidence intervals. Continuous predictors include log-transformed oxalate-extractable aluminum (log\_Al<sub>ox</sub>), soil pH, soil organic carbon (SOC), and clay content. Categorical variables (AEZ and geology) are expressed relative to their respective reference categories. The interaction term (log\_Al<sub>ox</sub> × pH) captures the conditional influence of oxide phases on P*



availability under varying soil chemical conditions. Significant effects ( $p < 0.05$ ) are highlighted in bold.



**Figure 1.** Spatial distribution of soil sampling locations across Nigeria overlaid on agroecological zones and underlying geological formations. Points represent sampled sites, while colored gradients indicate geological units. Agroecological zones are delineated by boundary lines, illustrating the strong climatic and pedogenic gradients across the country.

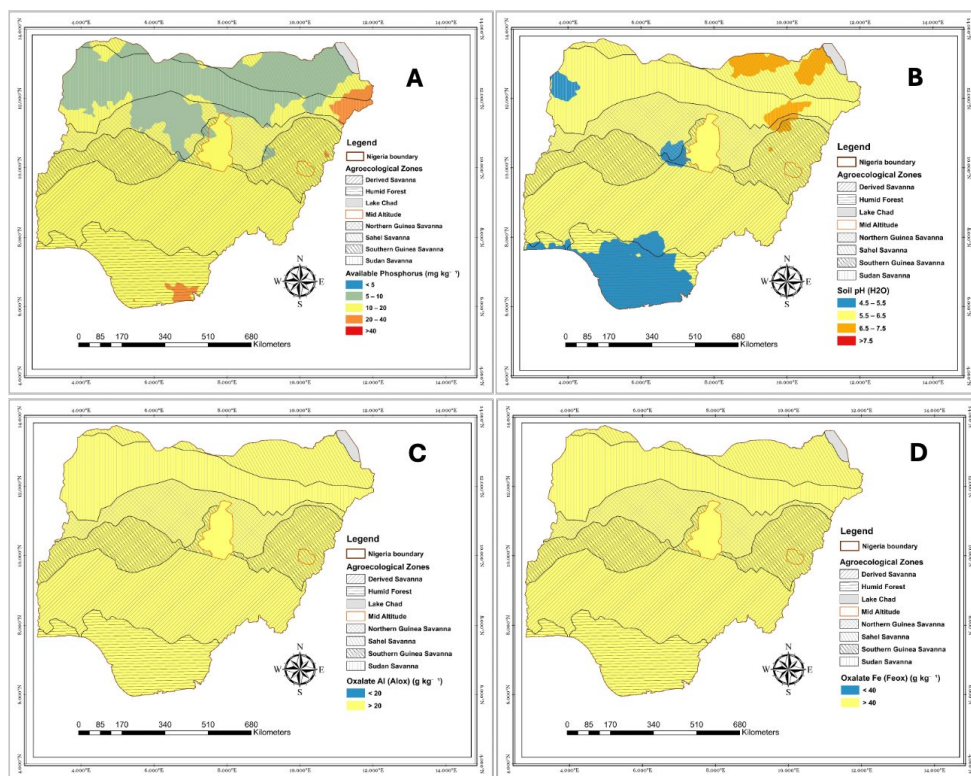


Figure 2. Distribution of available P (A), pH (B), and oxalate-extractable Al (C) and Fe (D) in top soils across Nigeria

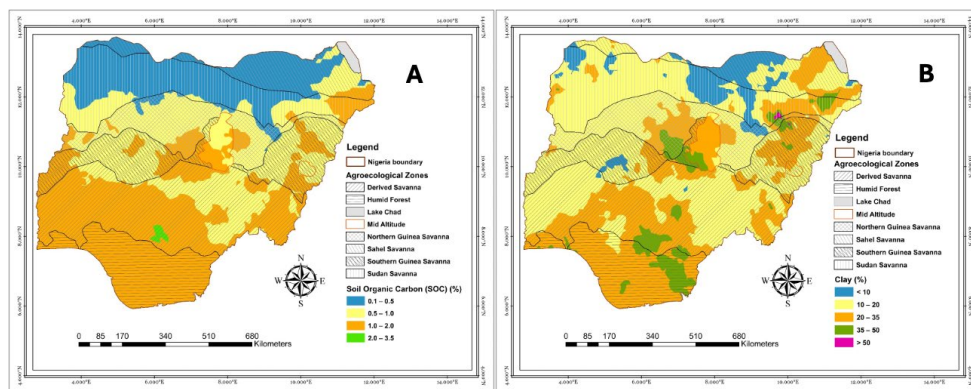


Figure 3: Distribution of SOC (A) and clay (B) in top soils across Nigeria

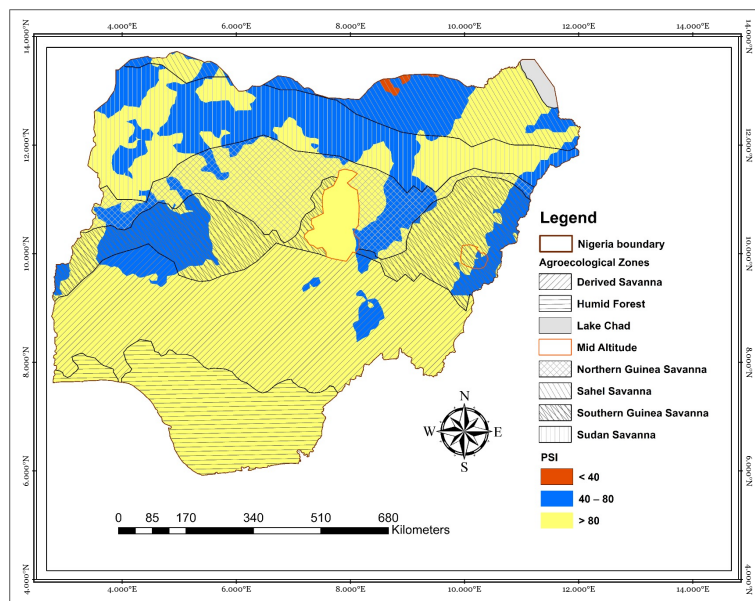


Figure 4: Map showing the distribution of phosphorus sorption index across Nigeria

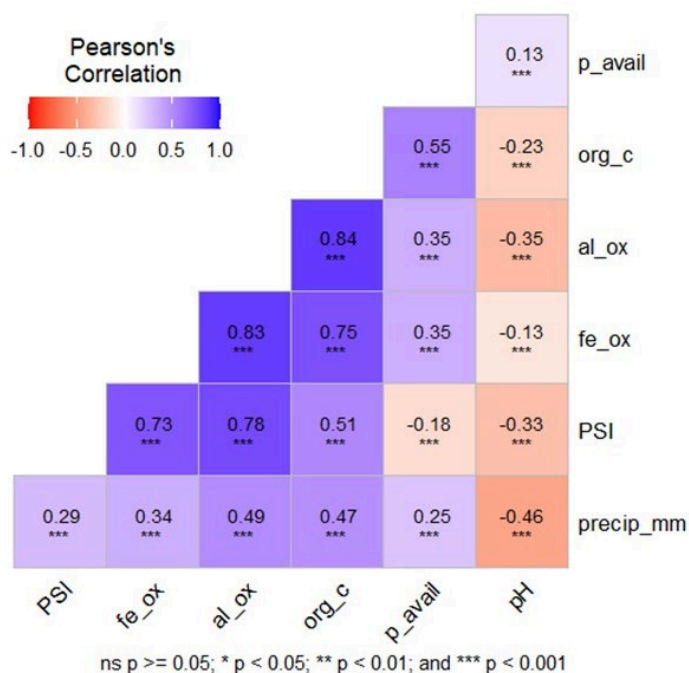


Figure 5: Correlation coefficient among the soil variables. Soil organic carbon (org\_c), precipitation (precip\_mm), soil pH, oxalate-extractable aluminum (al\_ox) and iron (fe\_ox), plant-available phosphorus (p\_avail), and phosphorus sorption index (PSI). Significant correlations were observed among the variables at  $p < 0.05$

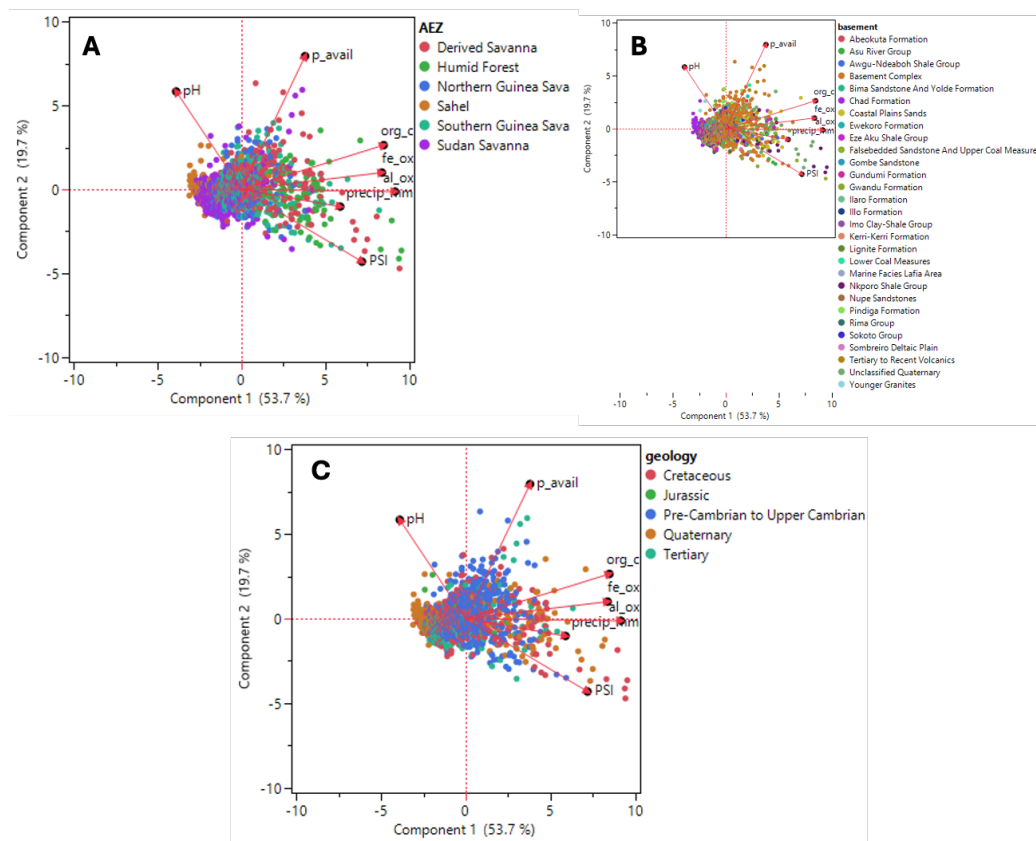


Figure 6: Biplot analysis of the soil variables based on agroecology (A) geological formations (B) and geological age (C). Soil organic carbon (org\_c), precipitation (precip\_mm), soil pH, oxalate-extractable aluminum (al\_ox) and iron (fe\_ox), plant-available phosphorus (p\_avail), and phosphorus sorption index (PSI).

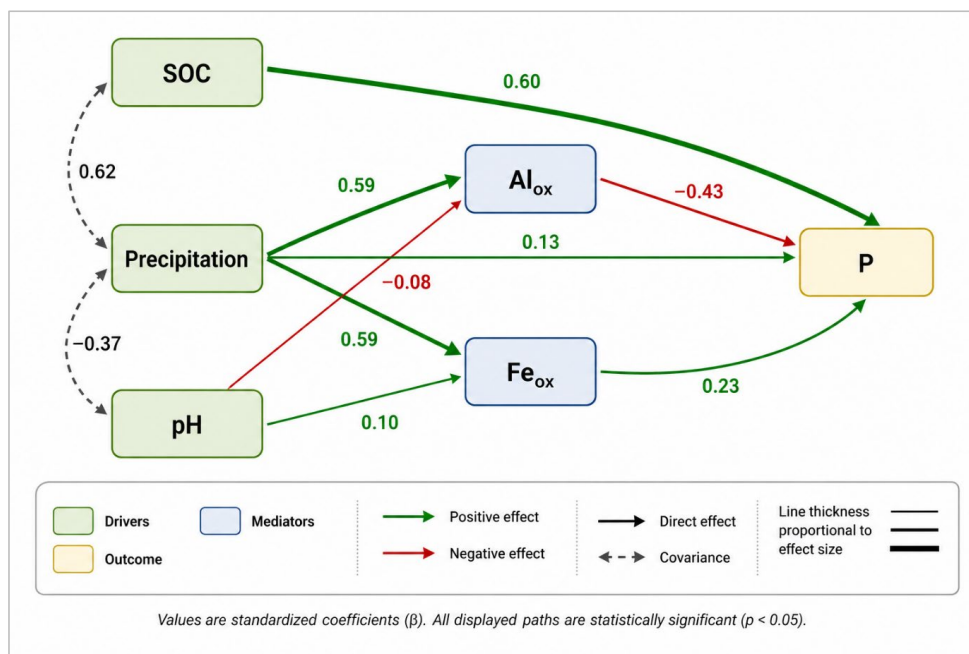


Figure 7: Structural equation model (SEM) illustrating the relationships among soil organic carbon (SOC), precipitation, soil pH, oxalate-extractable aluminum ( $Al_{ox}$ ) and iron ( $Fe_{ox}$ ), and plant-available phosphorus (P). Solid arrows indicate direct effects; dashed double-headed arrows represent covariances. Green arrows denote positive relationships, while red arrows indicate negative relationships. Arrow thickness is proportional to the magnitude of standardized path coefficients. Values alongside arrows are standardized coefficients ( $\beta$ ). All displayed paths are statistically significant ( $p < 0.05$ ).